

12

# EUROPEAN PATENT APPLICATION

21 Application number: 80200399.6

51 Int. Cl.<sup>3</sup>: H 01 M 8/04

22 Date of filing: 29.04.80

30 Priority: 02.05.79 NL 7903426

43 Date of publication of application:  
12.11.80 Bulletin 80/23

84 Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE

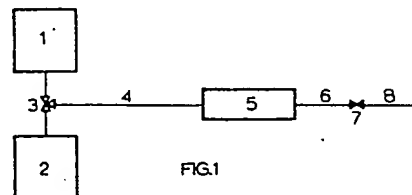
71 Applicant: Electrochemische Energieconversie  
N.V.(ELENCO N.V.)  
p/a SCK Eurochemic B 11  
B-2400 Mol(BE)

72 Inventor: Affenaar, Marinus  
Panoramaweg 6  
NL-6155 LZ Schinnen(NL)

74 Representative: Hoogstraten, Willem Cornelis  
Roeland et al,  
OCTROOIBUREAU DSM Postbus 9  
NL-6160 MA Geleen(NL)

54 Method for the operation of a fuel cell.

57 An improved method for operating a fuel cell with a porous gas diffusion electrodes to which an oxidizing or reducing gas is fed. The method provides for the regeneration of the electrode by keeping the oxidizing or reducing gas temporarily at a reduced concentration level while substantially maintaining the overall pressure of the gas phase in situ of the electrode and while continuing power offtake at least for the period during which the concentration level is reduced.



EP 0 018 693 A1

## METHOD FOR THE OPERATION OF A FUEL CELL

The invention relates to a method for the operation of a fuel cell with a porous gas diffusion electrode to which an oxidizing or reducing gas is fed, more in particular a method in which the electrode is regenerated and/or the fuel cell is put out of service for a prolonged stretch of time.

British Patent Specification 1,215,630 describes a method in which the polarization of a gas diffusion electrode is reduced by absorbing liquid electrolyte into the pores of the electrode. To this end the gas feed to the fuel cell is in an abrupt fashion temporarily reduced to zero thus to lower the pressure in the cell in such a way as to cause the electrolyte present in the cell to be drawn into the pores of the porous electrode. Such a process has the disadvantage that the carefully balanced three-phase equilibrium in the pores is disturbed. At the same time the proper operation of the fuel cell is disturbed, so that after treatment it is not readily restored to the proper stationary working condition. The sudden changes in pressure also constitute a major drawback, particularly if the fuel cells are composed to a battery. The control of the proper functioning of the battery as a whole is seriously hampered in that case.

The invention now provides a method which is free of these drawbacks. The method according to the invention is characterized in that the concentration of the oxidizing or reducing gas, calculated as molecular oxygen and hydrogen respectively, in the gas phase in situ of the electrode in question is temporarily brought to a reduced level, the overall pressure of the gas phase in situ of this electrode being substantially maintained and the power offtake, for at least the duration of the reduction of said concentration, being proceeded with. By this procedure the terminal voltage of the fuel cell is reduced, by preference, to below 10 % of the original value, more in particular to below 2 % of the original value.

The method according to the invention permits of the polarization of the porous gas diffusion electrode, which had gradually increased during operation of the fuel cell, to be substantially restored to the original level without putting the cell out of service and without the three-phase

equilibrium between gas, electrolyte and solid matter within the pores of the porous electrode being disturbed.

According to the invention fuel cells are preferably operated at operating pressures within 10 and 5000 kPa, although a higher or  
5 lower operating pressure is not excluded here. Operating pressures between 100 and 500 kPa are more particularly preferred. Suitable operating temperatures are 250-550 K, although higher and lower operating temperatures are not excluded. Practicable concentrations of the oxidizing gas, calculated as molecular oxygen, in the normal feed  
10 gas are 5-100 mol %, while the said reduced concentration level of the oxidizing gas preferably is 0-5 mol %. Highly suitable values for the concentration of the oxidizing gas in the normal feed gas are 15-100 mol % and for the reduced concentration level of the oxidizing gas 0-1 mol %. Suitable concentrations of the reducing gas, calculated as molecular  
15 hydrogen, are in the normal feed gas 5-100 mol %, while the said reduced concentration level of the reducing gas is preferably 0-5 mol %. Highly suitable values for the concentration of the reducing gas in the normal feed gas are 80-100 mol % and for the reduced concentration level of the reducing gas 0-1 mol %.

20 It is possible for the concentration level of the oxidizing or reducing gas in the gas phase in situ of the cathode or anode respectively to be reduced without reducing the overall pressure of this gas phase either by replacing the normal feed gas by a feed gas with a reduced concentration level of the oxidizing or reducing gas respec-  
25 tively but with the same overall pressure or by wholly or partially shutting off the spent gas discharge on the cathode or anode side respectively all the while proceeding with the power offtake, as a result of which the desired reduced concentration level of the oxidizing or reducing gas will adjust itself automatically.

30 Suitable feed gases with a normal concentration level of the oxidizing gas are air, oxygen-enriched air, pure oxygen, air diluted with nitrogen. Suitable feed gases with a reduced concentration level of the oxidizing gas are air, air diluted with nitrogen or another inert gas and inert gases such as nitrogen or the noble gases. Suitable feed  
35 gases with a normal concentration level of the reducing gas are hydrogen, hydrogen diluted with nitrogen, hydrogen diluted with carbon

dioxide. Suitable feed gases with a reduced concentration level of the reducing gas are hydrogen diluted with nitrogen and/or one or more other inert gases, and inert gases such as nitrogen or the noble gases.

According to one embodiment of the method according to the invention a fuel cell with a porous gas diffusion electrode is so  
5 operated that the electrode is regenerated at regular intervals by maintaining the concentration of the oxidizing or reducing gas in the gas phase in situ of the electrode for given periods at the said reduced level. Thus a gas of lower purity than would be required without appli-  
10 cation of this purifying method will suffice. Preferably the said concentration of the oxidizing or reducing gas is kept every 10-200 hours of service at the said reduced level for 1-30 minutes.

The method according to the invention is also highly suitable to take a fuel cell as described above out of service without injury to the quality of that cell. To this end the normal feed gas of the porous  
15 gas diffusion electrode of that cell is substituted by a gas substantially free of oxidizing or reducing gas respectively, such as nitrogen substantially free of oxygen or hydrogen respectively, without substantially changing the pressure in the gas phase in situ of the electrode,  
20 all the while continuing the power offtake. After a certain lapse of time the power offtake is stopped and the cell is stored until it is used again. It is also possible for the power offtake to be continued until the oxidizing or reducing gas is consumed and power generation comes to a standstill.

25 The method according to the invention is applicable for fuel cells employing all manner of porous gas diffusion electrodes. A suitable embodiment of the porous gas diffusion electrode is a flat electrode at least consisting of a catalytically active layer, which layer contains catalytically active metal, carbon and a polymer bonding  
30 agent and is porous to gas and electrolyte, with optionally an adjacent gas-permeable but liquid-tight layer. During operation the gas and liquid permeable layer is then in contact with the electrolyte, e.g. sodium or potassium hydroxide solution or a phosphoric acid solution. Suitable types of carbon for these gas diffusion electrodes are graphite, activated carbon, graphitized carbon, etc. Suitable bonding agents are polymeric materials such as polyethylene, polypropylene, polytetra-

fluoro-ethylene, polyvinyl chloride. Suitable catalytically active metals are nickel and noble metals such as iridium, rhodium, platinum, palladium, gold and alloys thereof. The porosity of the catalytically active layer can be enhanced by using soluble salts, such as sodium sulphate, sodium carbonate, ammonium carbonate and the like, as pore forming agents.

The method according to the invention is especially suited in the operation of gas diffusion cathodes in which oxygen is used as the oxidizing gas and in the operation of gas diffusion anodes in which hydrogen is used as the reducing gas.

The invention is now elucidated by means of the annexed drawings.

Fig. 1 represents a method according to the invention in which the concentration of oxidizing or reducing gas in the gas phase in situ of the electrode in question of a fuel cell is reduced by substituting a feed gas with a reduced concentration level of the oxidizing or reducing gas for the normal feed gas.

In the gas chambers 1 and 2 the same substantially constant pressure  $p$  obtains. One of the two gas chambers may communicate with the ambient air when oxidizing gas is supplied. Gas chamber 1 contains gas with a mol % oxidizing or reducing gas and gas chamber 2 with  $b$  mol % oxidizing or reducing gas, both calculated as molecular oxygen or hydrogen, where  $b$  is smaller than  $a$ .

Gas flows from gas chamber 1 via three-way valve 3 and gas supply line 4 to the porous gas diffusion electrode in question of fuel cell 5. Spent gas from the electrode is discharged from the cell via gas discharge line 6-8 with shutoff valve 7.

Once polarization of the electrode has exceeded a certain limit or after the lapse of a certain period of time, three-way valve 3 is switched so that gas starts to flow from gas chamber 2 to the porous gas diffusion electrode, the power offtake being continued. Owing to the continuing power offtake the oxidizing or reducing gas present in the gas phase in situ of this electrode is further spent and discharged. Thus the concentration of the oxidizing or reducing gas in the gas phase in situ of the electrode drops to a lower level. Restoring to the former operating condition is effected by switching three-way valve 3 back to

its original position.

With the arrangement described in Fig. 1 the fuel cell can also in a very suitable manner be put out of service for a prolonged period.

To this end gas chamber 2 is filled with a gas that is inert under the reaction conditions and does not contain oxidizing or reducing gas. A very suitable inert gas is nitrogen. The pressure in gas chamber 2 is again substantially constant and equal to that in gas chamber 1.

Three-way valve 3 is switched so that pure inert gas flows from gas chamber 2 to the porous gas diffusion electrode in question, the power offtake being continued. As the power offtake continues, the oxidizing or reducing gas present in the gas phase in situ of this electrode is spent and discharged and replaced by inert gas.

Thus a very low concentration of the oxidizing or reducing gas in the gas phase in situ of the electrode can be reached. After some time valve 7 is shut and the power offtake interrupted. If so desired, the power offtake can be proceeded with until the power generation comes to a standstill. The fuel cell can now be stored for a prolonged period and yet be taken into service at any time without any problem.

Fig. 2 illustrates another method according to the invention. This method employs only one feed gas for the relative electrode under all circumstances.

In gas chamber 1 a substantially constant pressure  $p$  obtains. If so desired this gas chamber 1 can communicate with the ambient air in the course of oxidizing gas being supplied. The gas chamber contains gas with a mol % oxidizing or reducing gas, calculated as molecular oxygen or hydrogen respectively.

From gas chamber 1 gas flows via valve 3 and gas supply line 4 to the porous gas diffusion electrode in question of fuel cell 5. Spent gas from the electrode is discharged from the cell via gas discharge line 6-8 with valve 7.

Once polarization of the electrode has passed a certain limit or after a given period of time has elapsed, valve 7 is fully or partially closed, the power takeoff being carried on. By the continuing power offtake, the oxidizing or reducing gas present in the gas phase in situ of this electrode is spent and, as the case may be, discharged, as a result of which the concentration of the oxidizing or reducing gas in the gas

phase in situ of the electrode drops to a lower level. Restoring to the former service condition is done by switching valve 7 back to its original position.

Preferably the last of these methods is at one given moment  
5 applied with either the cathode or the anode alone.

The invention is further elucidated by the following examples, without being restricted thereto.

#### Example 1

A hydrogen-air fuel cell was supplying current of density 1000  
10 A/m<sup>2</sup> at a corresponding terminal voltage of 0.69 Volts. The terminal voltage decreased with time to a value of 0.65 Volts.

The air stream over the cathode was replaced by an argon stream, the anode and cathode remaining short-circuited across a resistor. After 15 minutes, the original situation was restored. The terminal  
15 voltage at 1000 A/m<sup>2</sup> was again 0.69 Volts.

#### Example 2

A fuel cell was supplying power across a fixed resistor of 0.1 Ohm. Initially the power output amounted to 302 W. The cathodes of the fuel cell were fed with air at a constant rate of 1400 Nl/hour. The an-  
20 des were fed with hydrogen at a constant rate of 300 Nl/hour. After a certain lapse of time, the power output had decreased to 256 W.

The air discharge of the battery was then closed for 5 minutes. As a result the current dropped to substantially 0 A. When subsequently the air discharge was opened again, the battery resumed its supply of  
25 power within seconds. The power output across the resistor then amounted to 301 W.

#### Example 3

A hydrogen-air fuel cell battery with phosphoric acid electrolyte was fed at 175 °C with hydrogen containing 2 per cent by volume of  
30 CO. The anode contained noble-metal-on-carbon catalyst. In a few days time the voltage at which 800 A/m<sup>2</sup> could be supplied had decreased by 86 mV per unit.

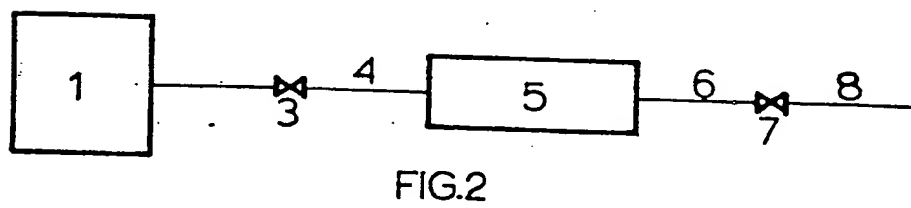
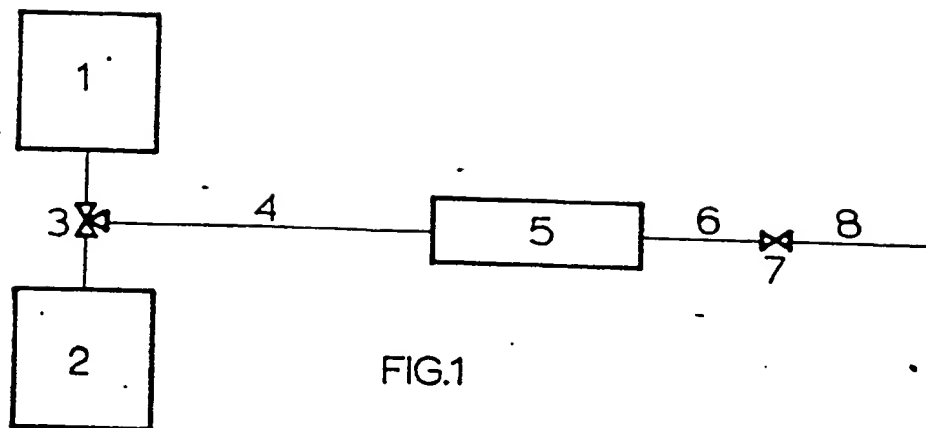
The hydrogen stream was replaced by a nitrogen stream, the battery being kept under load. The terminal voltage of the battery dropped to about 0.01 volt per cell unit and the current density decreased to substantially 0 A/m<sup>2</sup>. After 15 minutes the nitrogen stream was again replaced by a hydrogen stream. By this treatment, the battery voltage was so improved that the original voltage level at which 800 A/m<sup>2</sup> could be supplied was reached again but for 1 mV per cell unit.



C L A I M S

1. Method for the operation of a fuel cell with a porous gas diffusion electrode to which an oxidizing or reducing gas is fed characterized in that the concentration of the oxidizing or reducing gas, calculated as molecular oxygen or hydrogen respectively, in the gas phase in situ of the electrode in question is temporarily brought to a reduced level, the overall pressure of the gas phase in situ of this electrode being substantially maintained and the power offtake, for at least the duration of the reduction of the said concentration, being continued.
2. Method according to claim 1 characterized in that the porous gas diffusion electrode is regularly regenerated by maintaining the concentration of the oxidizing or reducing gas in the gas phase in situ of the electrode at given intervals and for a given time at the said reduced level.
3. Method according to claim 2 characterized in that during operation the said concentration of the oxidizing or reducing gas is maintained at the said reduced level for 1-30 minutes every 10-200 hours.
4. Method according to claim 1 characterized in that the fuel cell is taken out of service.
5. Method according to any of claims 1-4 characterized in that the concentration of the oxidizing or reducing gas in the gas phase in situ of the electrode in question is decreased by replacing the normal feed gas by a feed gas with a reduced concentration level of the oxidizing or reducing gas.
6. Method according to claim 5 characterized in that as the feed gas with reduced concentration level of the oxidizing or reducing gas a gas is employed that is inert under the conditions of the reaction.
7. Method according to claim 6 characterized in that nitrogen is used as the inert gas.
8. Method according to any of claims 1-3 characterized in that the resistance of the gas discharge line on the cathode or anode side of the fuel cell is increased without at least proportionally increasing the resistance of the gas feed line in question, the composition of the gas feed not substantially being changed.

9. Method according to any of claims 1-8 characterized in that it is used in the operation of gas diffusion cathodes employing oxygen as the oxidizing gas.
10. Method according to any of claims 1-8 characterized in that it is used in the operation of gas diffusion anodes employing hydrogen as the reducing gas.

$\frac{1}{1}$ 



European Patent  
Office

# EUROPEAN SEARCH REPORT

0018693

Application number

EP 80 20 0399

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. '1)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p><u>US - A - 3 644 148</u> (H. GUTBLER)</p> <p>* Claims 1,2,3; column 3, lines 25-63 *</p> <p>--</p> <p><u>FR - A - 1 281 168</u> (COMP. FR. THOMSON HOUSTON)</p> <p>* Page 1, left-hand column, line 18 - right-hand column, line 6; figure 6; page 5, left-hand column, line 29 - right-hand column, line 43 *</p> <p>--</p> <p><u>FR - A - 1 439 600</u> (UNITED AIR-CRAFT CORP.)</p> <p>* Page 3, right-hand column; figure 1; page 2, left-hand column, lines 23-26 *</p> <p>--</p> <p><u>GB - A - 1 296 831</u> (ENERGY CONVERSION)</p> <p>* Claims 1,3,5; page 2, lines 74-120 *</p> <p>--</p> <p><u>FR - A - 2 290 764</u> (INSTITUT FRANCAIS DU PETROLE)</p> <p>* Page 1, line 19 - page 2, line 8; page 4, line 10 - page 5, line 23; claims 1,2,3 *</p> <p>--</p> <p><u>FR - A - 2 353 142</u> (COMP. GEN. D'ELECTRICITE)</p> <p>* Claim 1 *</p> <p>--</p>	<p>1,4-7,9</p> <p>1,4-7,9,10</p> <p>1</p> <p>1</p> <p>1</p>	<p>H 01 M 8/04</p> <p>TECHNICAL FIELDS SEARCHED (Int. Cl. '1)</p> <p>H 01 M 8/04 8/08 8/00</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			<p>Δ: member of the same patent family, corresponding document</p>
Place of search		Date of completion of the search	Examiner
The Hague		12.08.1980	D'HONDT

0018693



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number:

EP 80 20 0399

-2-

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p><u>FR - A - 1 532 702 (SIEMENS)</u></p> <p>* Page 3, right-hand column, lines 37-55; figure 6; claims 1 and 5 *</p> <p>--</p>		
A	<p><u>US - A - 3 395 045 (P. REUTSCHI)</u></p> <p>* Claim 1 *</p> <p>----</p>		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

**THIS PAGE BLANK (USPTO)**